Preparation, Structure Characterization and Thermal Decomposition Process of the Dysprosium(III) m-Methylbenzoate 1,10-Phenanthroline Complex

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ABSTRACT

A dinuclear complex $[Dy(m\text{-}MBA)_3phen]_2 \cdot H_2O$ was prepared by the reaction of $DyCl_3 \cdot 6H_2O$, m-methylbenzoic acid and 1,10-phenanthroline in a 1:3:1 molar ratio, where m-MBA = m-methylbenzoate and phen = 1,10-phenanthroline. The complex was structurally characterized by single crystal X-ray diffraction, elemental analysis, UV and IR spectroscopy, molar conductance and TG-DTG techniques. It crystallizes in the monoclinic space group C_c with a = 15.962(16), b = 18.505(18), c = 22.547(2) Å; α = 90 °, β = 97.9820(10) °, γ = 90 °; z = 4. The unit cell contains a dinuclear molecule of the title compound. Each Dy(III) ion is eight-coordinated to one 1,10-phenanthroline molecule, one bidentate carboxylate group and four bridging carboxylate groups. The carboxylate groups are bonded to the dysprosium ions in two modes: chelating bidentate and bridging bidentate. The thermal decomposition process of $[Dy(m\text{-}MBA)_3phen]_2 \cdot H_2O$ has been followed by thermal analysis.

KEYWORDS

m-Methylbenzoic acid, 1,10-phenanthroline, dysprosium complex, crystal structure, thermal analysis.

1. Introduction

The complexes of rare earth ions and aromatic carboxylic acids have various coordination modes, and various crystal structures, which show interesting polymeric networks or chain structures.[1–3] They are used in many areas such as extraction and separation, germicides, catalysts, and functional materials. The nitrogen-containing ligand (phenanthroline or bipyridine) as a second ligand may strengthen conjugate function, enhance stability and reinforce ability of sterilization and fluorescence properties of the complexes. Therefore, many types of aromatic carboxylate lanthanide complexes with nitrogen-containing ligands were obtained[4–10] and their thermal decomposition behaviour has been reported in previous works.[11–15] As an extension, we now report the crystal structure and the thermal decomposition of $[Dy(m\text{-}MBA)_3phen]_2 \cdot H_2O$ by single crystal X-ray diffraction, elemental analysis, UV and IR spectroscopy, molar conductance and TG-DTG techniques. The information of thermal stability in air and spectral characteristics can provide theoretical foundations for the choice of functional complex materials.

2. Results and Discussion

2.1. Molar Conductivity

The molar conductivity (6.25 S cm² mol⁻¹) was determined in DMSO solution with DMSO as a reference. It is suggested that the complex $[Dy(m\text{-}MBA)_3phen]_2 \cdot H_2O$ is not an electrolyte.

2.2. Crystal Structure of $[Dy(m\text{-}MBA)_3phen]_2 \cdot H_2O$

The crystal data and structure refinement are given in Table 1. Selected bond lengths and angles are listed in Table 2. The struc-

ture of the complex $[Dy(m\text{-}MBA)_3phen]_2 \cdot H_2O$ is shown in Fig. 1. The packing diagram of the molecule in the crystal lattice is illustrated in Fig. 2.

In the crystal structure, the complex exists as a dinuclear compound. Each Dy(III) ion is coordinated by eight atoms, which include six oxygen atoms of the m-MBA ligands and two nitrogen atoms of the 1,10-phen molecule. The two Dy(III) ions are linked by the four bidentate bridge groups. This is similar to the case with the complexes $[Tb(m\text{-}MBA)_3phen]_2 \cdot (H_2O)_2$[16] and $[Eu(m\text{-}MBA)_3phen]_2 \cdot (H_2O)_2$,[17] but the structures of the coordination polyhedra of the metal ions are different. The title complex shows a distorted dodecahedron arrangement (see Fig. 3), while the complex $[Eu(m\text{-}MBA)_3phen]_2 \cdot (H_2O)_2$ presents a distorted square antiprism geometry.[17]

In the dinuclear molecule, the Dy-O bond distance formed by the bridging carboxylates is slightly shorter than that formed by the chelating carboxylate groups. The Dy-O bond lengths are in the range of 2.280 to 2.457 Å (Table 2), with a mean bond length of 2.346 Å; and Dy-N bond lengths are in the range of 2.546 to 2.620 Å (Table 2), with an average distance of 2.583 Å. They are also slightly shorter than the corresponding average distances of the complexes $[Tb(m\text{-}MBA)_3phen]_2 \cdot (H_2O)_2$[16] (2.380 Å and 2.595 Å) and $[Eu(m\text{-}MBA)_3phen]_2 \cdot (H_2O)_2$[17] (2.389 Å and 2.599 Å), which can be possibly explained by the radii of the metal ions.

2.3. IR Spectra

The characteristic absorption band attributed to COOH in the free acid ligand is observed at 1690 cm⁻¹, but is not observed in the complex. The IR spectrum of the complex showed absorption bands at 1585–1555 and 1400–1360 cm⁻¹, which are attributed to the antisymmetric and symmetric vibrations of the COO⁻ groups. The absorption band at 556–425 cm⁻¹ is assigned to the

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Table 1 Crystal data and structure refinement for [Dy(m-MBA)$_3$phen]$_2$·H$_2$O.

Item	Data
Empirical formula	C$_{72}$ H$_{60}$ Dy$_2$ N$_4$ O$_{13}$
Formula mass/g mol^{-1}	1514.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C$_c$
Unit cell dimensions	a = 15.962 (16) Å α = 90 °
	b = 18.505(18) Å β = 97.9820 (10) °
	c = 22.547(2) Å γ = 90 °
Volume	6595.5(11) Å^3
Z, calculated density	4, 1.53 g cm^{-3}
Absorption coefficient	2.32 mm^{-1}
F(000)	3024
Crystal size	0.32 ×0.26 ×0.22 mm
Theta range for data collection	2.01 to 25.03 °
Limiting indices	–12 ≤ h ≤ 18, –22 ≤ k ≤ 22,
	–26 ≤ l ≤ 26
Reflections collected/unique	17708/8692 [R$_{(int)}$ = 0.0237]
Completeness to theta = 25.03	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.62
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8692/2/834
Goodness-of-fit on F^2	1.047
Final R indices [I>2σ(I)]	R_1 = 0.0227, wR_2 = 0.0498
R indices (all data)	R_1 = 0.0269, wR_2 = 0.0511
Absolute structure parameter	–0.013(6)
Largest diff. peak and hole	0.354 and –0.382 e Å^{-3}

Table 2 Bond lengths/Å and angles/° for [Dy(m-MBA)$_3$phen]$_2$·H$_2$O.

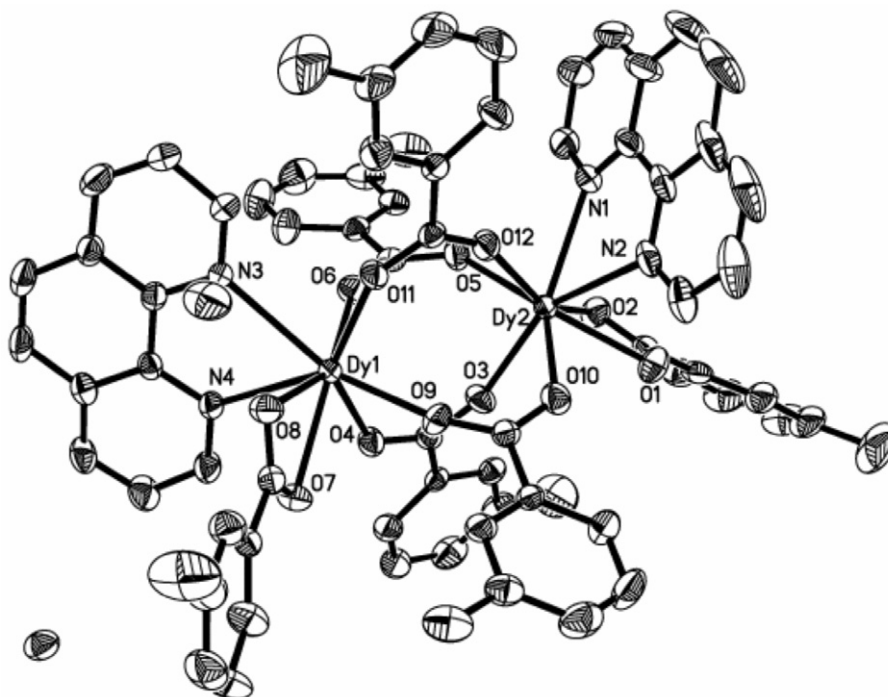|			
Dy(1)-O(6)	2.280(4)	Dy(2)-O(1)	2.388(4)
Dy(1)-O(9)	2.287(3)	Dy(2)-O(2)	2.457(4)
Dy(1)-O(11)	2.308(3)	Dy(2)-N(1)	2.569(5)
Dy(1)-O(4)	2.337(4)	Dy(2)-N(2)	2.578(4)
Dy(1)-O(8)	2.432(4)	Dy(2)-O(3)	2.284(3)
Dy(1)-O(7)	2.432(3)	Dy(2)-O(10)	2.299(4)
Dy(1)-N(4)	2.564(4)	Dy(2)-O(12)	2.299(4)
Dy(1)-N(3)	2.628(4)	Dy(2)-O(5)	2.311(4)
O(6)-Dy(1)-O(9)	113.02(13)	O(10)-Dy(2)-O(5)	137.53(13)
O(6)-Dy(1)-O(11)	82.26(13)	O(12)-Dy(2)-O(5)	80.94(15)
O(4)-Dy(1)-O(8)	129.47(12)	O(3)-Dy(2)-O(1)	90.90(14)
N(4)-Dy(1)-N(3)	63.06(13)	O(10)-Dy(2)-O(1)	77.57(15)

line to Dy(III).[18] These results are in agreement with those of the crystal structure of the complex.

2.4. UV Spectra

The UV spectra of two ligands and the complex were determined in DMSO solution with DMSO as a reference. The strong absorption band of m-methylbenzoic acid at 258 nm shifts to 265 nm in the complex. This may be caused by the expansion of the π-conjugated system after coordination with the Dy(III) ion.[19] The strong absorption band of the 1,10-phenanthroline complex at 265 nm is similar to that in the free base. This is because the conjugated system of 1,10-phenanthroline coordinated to the metal ion does not change compared with that in 1,10-phenanthroline itself.

2.5. Thermogravimetric Analysis

The TG-DTG curves of [Dy(m-MBA)$_3$phen]$_2$·H$_2$O with a heating rate of 10 °C min^{-1} are illustrated in Fig. 4. There are three main mass loss steps on heating from 25 to 900 °C. In the first stage, 1.15 % of the mass was lost in the range of 27–81 °C, which is ascribed to the release of a water molecule from the complex (theoretical mass loss is 1.2 %). The second stage started at 267 °C and ended around 420 °C, with a mass loss of 23.77 %, corresponding to the loss of two phen molecules (theoretical loss is

metal-oxygen ionic bond, suggesting that the carboxylate groups are coordinated to the Dy(III) ion.[18] In contrast to the absorption bands found at 1562 cm^{-1} and 1447 cm^{-1} in the 1,10-phenanthroline ligand due to the stretching vibrations of the C=N group, these bands shift to lower wavenumber (1558 cm^{-1} and 1417 cm^{-1}) in the spectrum of the complex, reflecting the coordination of the nitrogen atoms of 1,10-phenanthro-

Figure 1 Structure of the complex [Dy(m-MBA)$_3$phen]$_2$·H$_2$O.
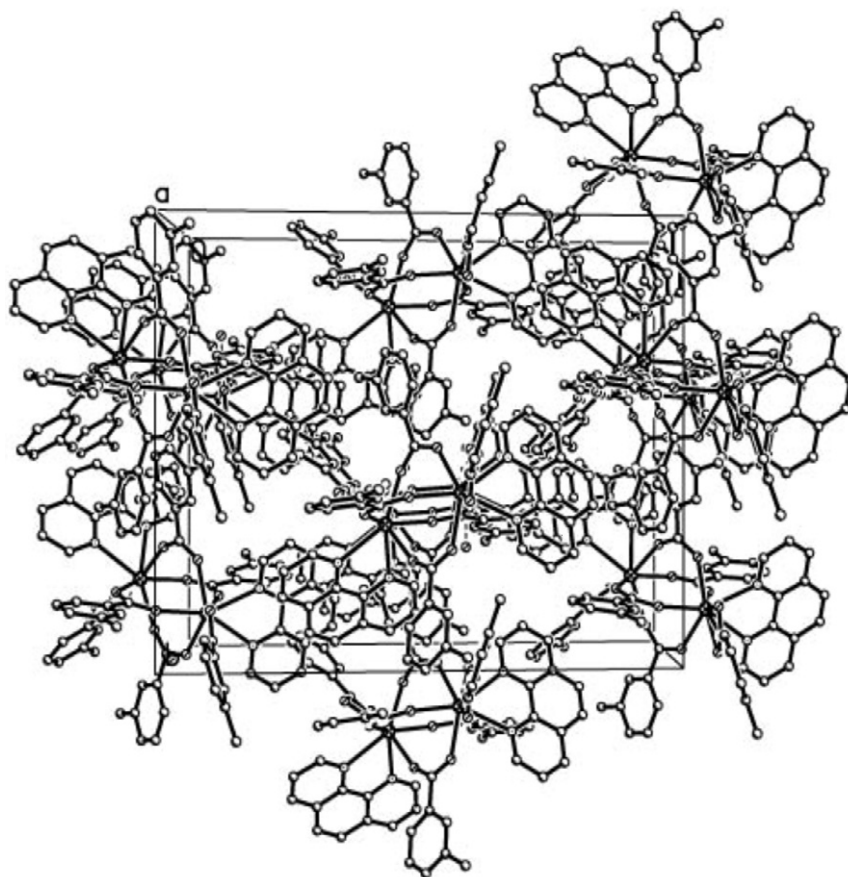
Figure 2 Packing diagram of the complex [Dy(m-MBA)$_3$phen]$_2$·H$_2$O.

23.8 %). The IR spectra of the residue at 420 °C shows that the absorption band of the C=N group at 1558 cm^{-1} disappears. The last stage of mass loss is from 459 to 822 °C, with a mass loss of 49.11 %, which is attributed to the further decomposition of the complex. The residue amounted to 24.05 %, which is Dy$_2$O$_3$ (calculated: 24.6 %). The IR spectrum of the residue is the same as that of a genuine Dy$_2$O$_3$ sample. In addition, from the TG-DTG curves, it is found that there are two consecutive steps in the second stage and the third stage respectively, but there are no clear plateaus in the TG curve, indicating that the intermediate products are unstable.

On the basis of the experimental and calculated results, the thermal decomposition process is represented as follows.

[Dy(m-MBA)$_3$phen]$_2$·H$_2$O → [Dy(m-MBA)$_3$phen]$_2$ →
[Dy(m−MBA)$_3$]$_2$ → Dy$_2$O$_3$
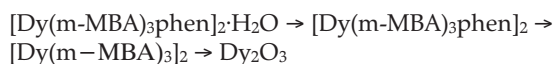
3. Experimental

3.1. Materials and Apparatus

All the regents used were analytical grade without further purification.

Analyses of C, H, and N were performed on a Carlo-Erba model 1106 elemental analyser. Infrared spectra of KBr pellets were recorded in the range of 4000–400 cm^{-1} on a Bio-Rad FTS-135 spectrometer. TG and DTG experiments were performed using a Perkin-Elmer TGA7 thermogravimetric analyser with a heating rate of 10 °C min^{-1} under static air atmosphere. UV spectra were recorded using a Shimadzu 2501 spectrometer. Molar conductivities were determined with a DDS-307 conductometer, supplied by Exactitude Apparatus, Shanghai. X-ray diffraction data were obtained using a Bruker Apex II CCD

diffractometer with graphite-monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å) at 293 K. A semi-empirical absorption correction based on SADABS was applied. Unique data (R$_{int}$ = 0.0237) were used to solve the structure by direct methods using the SHELXS-97 program,[20] and refined on F^2 by full-matrix least-squares methods using the SHELXL-97 program.[21]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-293425. Copies of the data can be obtained free of
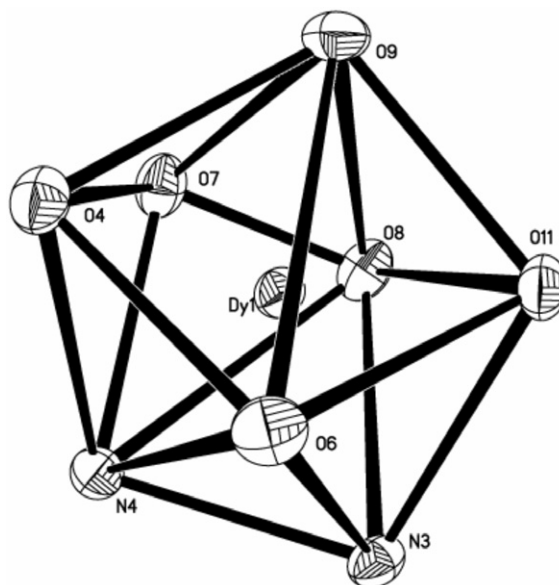

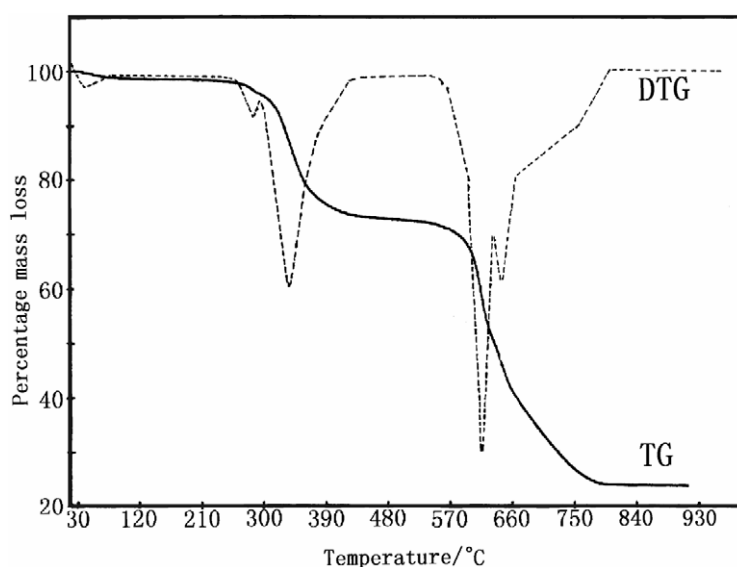**Figure 3** Coordination polyhedron of the Dy(III) ion.

Figure 4 TG-DTG curves of [Dy(m-MBA)$_3$phen]$_2$·H$_2$O.

charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +(1223)-336033; e-mail for enquiries: fileserv@ccdc.cam.ac.uk).

3.2. Synthesis

The mixture of m-methylbenzoic acid (0.2042 g, 1.5 mmol) and 1,10-phenanthroline (0.0991 g, 0.5 mmol) was dissolved in an appropriate amount of ethanol and the pH was adjusted to 6–7 by using 1.0 mol L^{-1} NaOH solution. DyCl$_3$+6H$_2$O solution was obtained by dissolving Dy$_2$O$_3$ in HCl (6.0 mol L^{-1}). Then the mixture was slowly dropped into the DyCl$_3$+6H$_2$O solution, and a white precipitate appeared instantly. After stirring and deposition at room temperature, the precipitate was filtered off, washed with deionized water and ethanol, dried and stored. By slow evaporation of the solvent at room temperature, colourless single crystals were obtained after four weeks. Yield: 78.8%. UV/vis: λ_{max} = 265 nm (log ε = 0.39). IR (film): $\tilde{\nu}$ = 1583 (C$_{26}$, C$_{27}$), 1558 (C$_{13}$, N$_3$), 1417 (C$_{24}$, N$_3$), 420 (Dy, O) cm^{-1}. (Found: C 56.99, H 3.40, N 3.77, Dy 21.16. Calc. for C$_{72}$H$_{60}$Dy$_2$N$_4$O$_{13}$ (1514.24): C 57.10, H 3.99, N 3.70, Dy 21.46).

4. Conclusions

In summary, the title complex has been successfully synthesized, and the crystal structure was determined by single crystal X-ray diffraction. Dy^{3+} is eight-coordinated with a distorted dodecahedron arrangement. The thermal decomposition of the complex [Dy(m-MBA)$_3$phen]$_2$·H$_2$O occurs in three steps, and the process is shown in the text.

Acknowledgements

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